



Inhibiting effect of decanoic acid and its by-products on the transformation of *n*-hexadecane over a Pt/SiO₂-Al₂O₃ catalyst



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ABSTRACT

The impact of decanoic acid (a model molecule representative of the most abundant oxygenates present in LTFT syncrude) and its by-products (CO, CO₂, H₂O) on the transformation of *n*-hexadecane was studied over a Pt/Al₂O₃-SiO₂ conventional bifunctional catalyst under hydrocracking conditions. An irreversible impact of decanoic acid and its by-products (CO and CO₂, H₂O) was demonstrated corresponding to a decrease of the activity of the catalyst and a modification of the selectivities towards isomerization and cracking. Water produced by the total transformation of the acid, CO, CO₂ was identified as the real contaminant whatever the oxygenates. The catalyst selectivities towards isomerization and cracking were modified in favour of isomerization in the presence of low amounts of oxygenates. The balance (acid and hydro-dehydrogenation properties) of the catalyst was modified corresponding to a decrease of the acidity of the support and a sintering of the platinum.

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1. Introduction

With the emergent need to get less dependent of fossil fuels, biomass seems to be a good answer, growing every day and conquering a significant position in this field. The constant evolution of quotidian life needs in the developed countries and the energy demand of the growing economies are a strong incentive for the search for new resources. The main reasons are economical, due to the practiced prices and the associated costs, and environmental, in order to progress in a sustainable world development and to preserve it. The production of liquid fuels through the Fischer-Tropsch (F-T) process appears as a new way for the valorization of biomass. It is also well documented that the diesel fuels produced by the Low Temperature F-T (LT F-T) process offer significant advantages over those derived from crude oil, such as a much higher cetane number (typically above 70) due to their high concentration of linear paraffins, and the almost absence of sulphur, nitrogen and aromatics, resulting in a reduced emission of pollutants to the atmosphere [1–9]. However, this resulting diesel has some constraints asso-

ciated, like the highly paraffinic nature of the F-T products that confers to the diesel fuel unacceptable low cold flow properties for commercial purposes; and the impossibility of obtaining a product with a narrow chain-length range, since F-T synthesis follows a statistical distribution of hydrocarbons known as the Anderson-Schulz-Flory or ASF distribution [3,10,11]. Production of diesel fuels can be achieved by the catalytic hydroconversion of the heaviest part of the FT paraffinic product (waxes). Hydroconversion of such process involves the use of bifunctional hydroisomerization and hydrocracking catalysts. Hydrocracking catalysts contain a hydro-dehydrogenating function provided by a metal phase (platinum, palladium, ...) or by metal sulfides of groups VI and VIII (type "NiMoS" "NiWS" ...) and a Brønsted acidic function provided by typically a zeolite (usually Y-type) or an amorphous silica-alumina [12]. The hydroisomerization and hydrocracking of normal paraffins have been the subject of many academic studies since the original work of Weisz and of Coonradt and Garwood in the sixties [13,14]. The most commonly accepted mechanism involves first that the *n*-paraffin is dehydrogenated to the *n*-olefin on the hydro/dehydrogenating sites and is then after protonated in carbenium ion on the acid sites. After structural rearrangement and/or β-scission, the carbenium ions desorb in the form of olefins after deprotonation on the acid sites. Then, after diffusion to the hydro-

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dehydrogenating sites, olefins are hydrogenated to form the final reaction products. When maximum diesel selectivity is desired, it is necessary to minimize the multiple cracking reactions on the acid sites. When the overall reaction rate is controlled solely by the steps catalyzed by the acidic function, the bifunctional catalyst is called “ideal”. In the case of hydrocracking of Fischer-Tropsch waxes, it is usually suggested to use a noble metal catalyst supported on a mesoporous support with moderate acidity, such as silica-alumina [14]. It is easily understood that the presence of inhibitors (poisons) in the feed to be treated can not only greatly affect the catalyst activity, but also its selectivity when the inhibitor is specific to one of the two functions and therefore modifies the balance between the activities of the hydro-dehydrogenating and acidic functions. This is well known in the case of the conventional vacuum gas oil hydrocracking which is carried out in the presence of ammonia (inhibitor of acid sites) and hydrogen sulfide (noble metal poison and sulfide phase inhibitor) [10]. The Fischer-Tropsch waxes systematically contain oxygenated compounds [10]. Their detailed composition has also been carried out very recently using gas chromatography in two dimensions [10,15]. These compounds are the aliphatic alcohols, carboxylic acids, aldehydes and esters, with a typical overall weight content of a few percent [10]. Studies about the reactivity and impact of these oxygenated compounds on hydrocracking catalysts are scarce and this point can be of crucial importance, as both the activity and selectivity of the catalysts towards liquid fuels can be affected. In the literature, few authors showed that alcohols, acids and oxygenated compounds can interact with acid sites [16–21]. In this case, the acidic function of hydrocracking catalysts can be impacted by the presence of oxygenates.

Leckel [5] reported that the presence of tetradecanol and lauric acid during hydrocracking of FT wax over a Pt/W/SiO₂-Al₂O₃ catalyst could change the acid-metal balance of the original catalysts by competitive adsorption on the active sites, and each family of oxygenated product would adsorb preferentially on a different function. Alcohols would adsorb preferentially on the acid sites, increasing the metal-to-acid sites ratio while carboxylic acid would decrease this ratio by adsorbing preferentially on the metallic sites. Guedes et al. [22], in the same way, showed that the presence of decan-1-ol inhibited the transformation of *n*-hexadecane, a model molecule representative of the long chain paraffins produced from LT F-T and also the selectivities towards isomerization and cracking in favour of isomerization over a Pt/silicated alumina catalyst. The authors explained these results by an irreversible modification of the catalyst by water which was found to be the real contaminant.

The aim of this work is to establish and to understand the impact of other model oxygenated compounds on the hydrocracking of a long chain *n*-alkanes produced in LT F-T process over a Pt supported over silicated alumina conventional bifunctional catalyst. Decanoic acid was chosen as a model molecule representative of the carboxylic acid and *n*-hexadecane as the model molecule representative of the long chain paraffin as reported in literature [15,22]. The decanoic acid and its oxygenated by-products (CO, CO₂) impact on the hydroconversion of *n*-hexadecane performed over a con-

Table 1

Physical properties of the Pt/silicated alumina hydrocracking catalyst.

Catalyst properties	
Pt (wt.%)	0.48
Pt dispersion (%)	85
SiO ₂ /Al ₂ O ₃ (%wt)	30/70
BET surface area (m ² g ⁻¹)	297

ventional Pt/silicated alumina hydrocracking catalyst was studied under typical hydrocracking conditions. Moreover, the catalyst acidic and metallic functions were characterized before and after the introduction of the oxygenates in order to understand the modification of the catalyst induced by their presence. These results are compared to those previously obtained by Guedes et al. [22] in the same operating conditions for the impact of decan-1-ol and water for the hydroconversion of *n*-hexadecane.

2. Experimental

2.1. Catalyst characterization

A Pt supported over silicated alumina catalyst (30%SiO₂-70%Al₂O₃) (supplied by IPFEN) was used for the catalytic tests; physical properties are listed in Table 1. The catalyst was crushed and sieved in the range of particles size from 0.250 to 0.315 mm for the catalytic test.

2.2. Reaction conditions

As described previously [22], catalytic activity measurements were carried out in a fixed-bed reactor at 608 K under a total pressure of 5 MPa, which was typically loaded with 1 g of catalyst. First of all, the catalyst was dried *in situ* at 423 K for 1 h in nitrogen flow (6 NL g_{catalyst}⁻¹ h⁻¹) and then reduced under atmospheric pressure in H₂ flow (6 NL g_{catalyst}⁻¹ h⁻¹) at 723 K for 2.5 h. The desired reaction conditions were adjusted (608 K, 5 MPa) and then the model feed was injected into the reactor. An H₂/feed molar ratio of ~13 was used and the Weight Hourly Space Velocity (WHSV, ratio between the *n*-C₁₆ mass flow and the catalyst mass) varied from 20 to 2.2 h⁻¹ (corresponding to 1/WHSV varied from 0.05 to 0.45 h, residence time) when pure hexadecane was used. Various model feeds were injected, pure *n*-hexadecane (*n*-C₁₆, from Aldrich, 99+% purity), decanoic acid (98+% purity, purchased from Alfa Aesar, 5 wt.% in *n*-heptane, purchased from Aldrich) or *n*-hexadecane spiked with various amounts of decanoic acid (from 0.5 to 2 wt.%) or its transformation products (CO or CO₂: from 2 kPa and 9 kPa, 1% or 10% in H₂ from Air Liquid). The various partial pressures depending on the model feed are reported in Table 2.

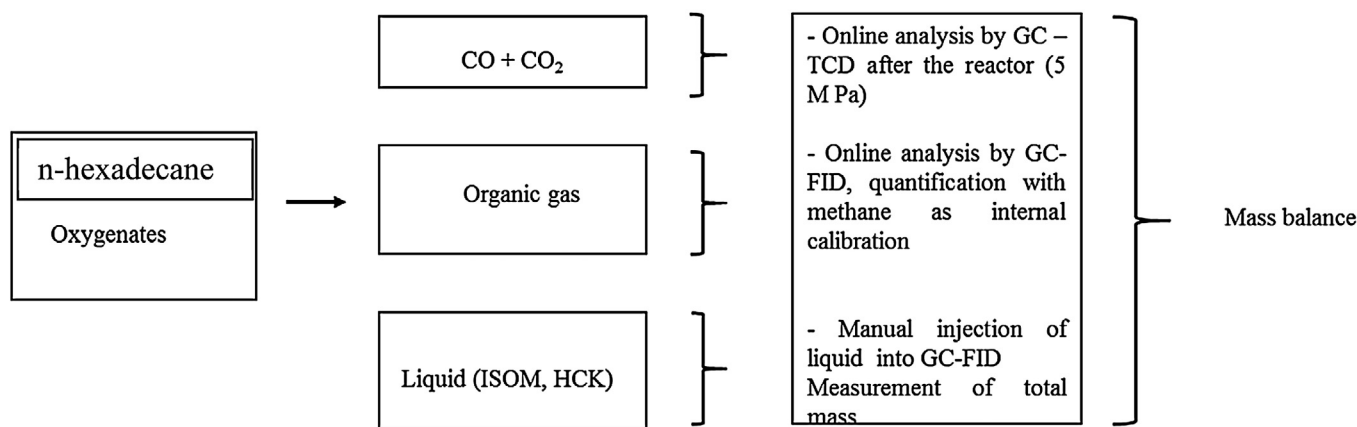
The experimental procedure to study the impact of the oxygenates (decanoic acid, CO or CO₂) is presented below:

Step A: Hydroconversion of *n*-C₁₆ (70% of conversion in order to evaluate the isomerization and cracking properties, (1/WHSV = 0.2 h));

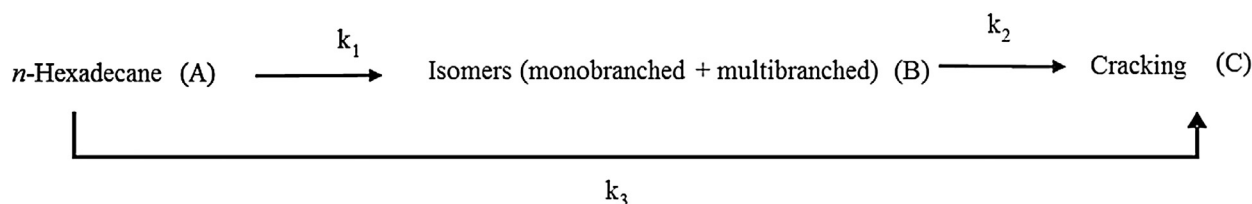
Table 2

Partial pressures of the different compounds depending on the model feed. (P = 5 MPa, T = 608 K).

Feed	P _{H2} (MPa)	P _{n-C16} (MPa)	P _{n-C7} (MPa)	Oxygenates	
				P (kPa)	wt%
<i>n</i> -Hexadecane alone	4.64	0.36	0	0	0
<i>n</i> -Heptane + decanoic acid	4.64	0	0.35	10–11	1 and 5
CO alone	4.99–5.00	0	0	2–9	–
CO ₂ alone	4.99–5.00	0	0	2–9	–
<i>n</i> -Hexadecane + Decanoic acid	4.64	0.35–0.36	0	2–9	0.5–2
<i>n</i> -Hexadecane + CO	4.64	0.35–0.36	0	2–9	802–3332 ppm
<i>n</i> -Hexadecane + CO ₂	4.64	0.35–0.36	0	2–9	1260–5236 ppm



Scheme 1. Methodology of the global mass balance measurement.



Scheme 2. Transformation of *n*-hexadecane over Pt/silicated alumina catalyst (P = 5 MPa, T = 608 K).

Step B: Hydroconversion of *n*-C₁₆ spiked with various amounts of decanoic acid or CO or CO₂ at the same contact time of step A;

Step C: *Re-establish* operating conditions of step A (return point: RP) to quantify the degree of deactivation of the catalyst.

The transformation of decanoic acid alone has also been studied (5 wt.% diluted in *n*-heptane), under hydrocracking conditions (608 K, 5 MPa, H₂/feed mole ratio of ~13, 1/WHSV = 0.058 h with respect to decanoic acid) over the catalyst and also over the support. Under these conditions, the conversion of *n*-heptane is lower than 3 wt.%. The transformation of CO and CO₂ alone were studied in the same operating conditions and for partial pressures (from 2 kPa to 9 kPa) corresponding to the transformation of decanoic acid.

For a given operating condition, Pt/silicated alumina catalyst was rapidly stable (typically after 1 h time on stream) and no deactivation was observed.

2.3. Analysis

Under these experimental conditions, a mixture of gas and liquid was present at the outlet of the reactor. The gas phase was analyzed *online* by means of a Varian gas-chromatograph equipped with an automatic sampling valve, a Supelco Petrocol capillary column (DH 50.2, 50 m × 0.2 mm × 0.5 μm film) and a flame ionization detector. Owing to the high boiling point of the reactants, online analysis of the reaction products was not convenient. Consequently, the reactor effluents were condensed and liquid samples were periodically collected (every hour) to be analyzed by gas chromatography. The carrier gas was hydrogen and the analytical conditions were adjusted to obtain the accurate separation namely an *inlet* pressure of 80 kPa and a temperature of 573 K for the injector and the detector. The temperature program used was as follows: from 318 to 348 K (2 K min⁻¹) and 318 K to 493 K (2 K min⁻¹) to analyze the gas and the liquid phase respectively. The quantification of the gas phase formed during the hydrocracking of *n*-C₁₆ was made by calibrating the gas with an external standard (methane). The response factors for hydrocarbons are around 1. Carbon monoxide, carbon dioxide and methane have been analyzed online by a Varian 3900

chromatograph equipped with an automatic sampling valve, two Porapack columns 1 m × 1/8" × 2 mm, and a thermal conductivity detector. A backflush procedure allowed the elimination of the organic compounds. The analysis conditions were a temperature of 313 K for the oven, 423 K for the detector and a sensitivity of 0.05.

2.4. Calculations

The mass balance (MB) for each experiment was calculated from the ratio between the mass of the liquid products (*m*_{liq}) and of collected gas (*m*_{gas}) and the mass of feedstock injected (*m*_{injected}):

$$MB(\%) = \left(\frac{m_{liq} + m_{gas}}{m_{injected}} \right) \times 100$$

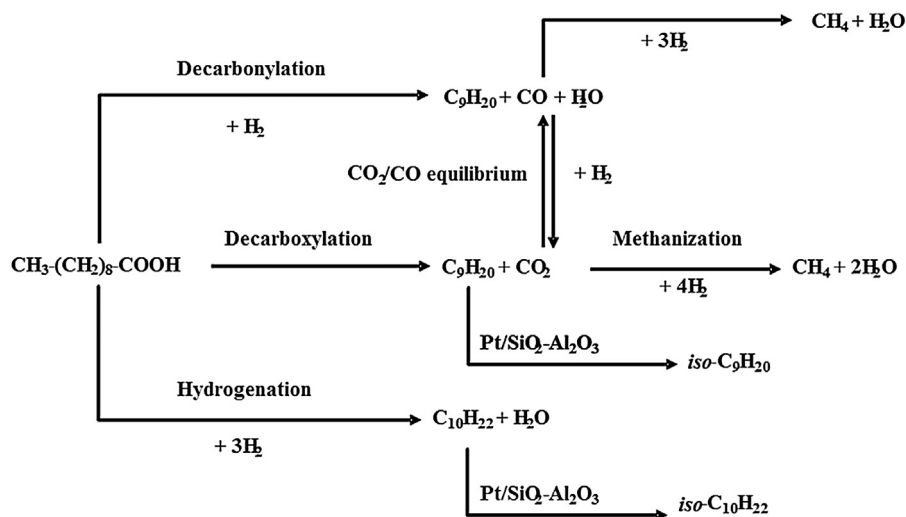
The mass balance calculation methodology is depicted in Scheme 1. The mass balance was found to be 100 ± 2.5% in all cases.

The results were expressed and analyzed as follows:

The conversion of *n*-C₁₆ (C), taking into account the gas and the liquid phases, has been calculated:

$$C(\text{wt}\%) = \left(\frac{\left(\frac{\sum A_{iso-C_{16}} + \sum_{n=1}^{15} A_{C_n}}{\sum_{n=1}^{16} A_{C_n}} \right) \times m_{liq} + m_{gas}}{m_{liq} + m_{gas}} \right) \times 100$$

where $\sum A_{C_n}$ is the sum of area for all hydrocarbons with *n* carbon atoms and $\sum A_{iso-C_{16}}$ is the sum of area corresponding to the isomerization of *n*-hexadecane. For feedstocks containing oxygenates,



Scheme 3. Transformation of decanoic acid over Pt/silicated alumina catalyst ($P = 5$ MPa, $T = 608$ K).

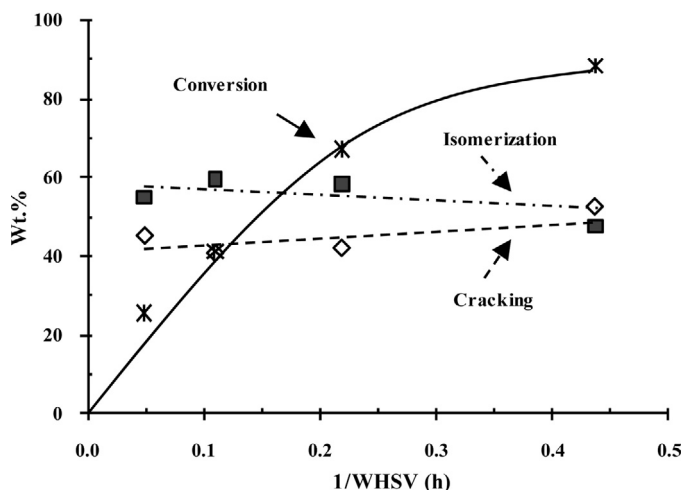


Fig. 1. Transformation of *n*-hexadecane. Conversion and selectivities towards isomerization and cracking, as a function of $1/WHSV$ ($P = 5$ MPa, $T = 608$ K, $H_2/\text{feed} = 13$ mol/mol, Pt/silicated alumina).

hydrocarbons resulting from the oxygenates decomposition are excluded from the calculation.

Hydroisomerization (Y_{isom}) and hydrocracking (Y_{Cr}) yields were calculated according to:

$$Y_{\text{isom}}(\text{wt.}\%) = \frac{\sum_{n=1}^{16} A_{\text{isoC}_{16}}}{\sum_{n=1}^{16} A_{\text{C}_n}} \times 100$$

$$Y_{\text{Cr}}(\text{wt.}\%) = \frac{\sum_{n=1}^{15} A_{\text{C}_n}}{\sum_{n=1}^{16} A_{\text{C}_n}} \times 100$$

The hydroisomerization (S_{isom}) and hydrocracking selectivities (S_{Cr}) were calculated by the ratio between the corresponding yield and the *n*-C₁₆ conversion. For feedstocks containing oxygenates, hydrocarbons resulting from the oxygenates decomposition are excluded from the calculation.

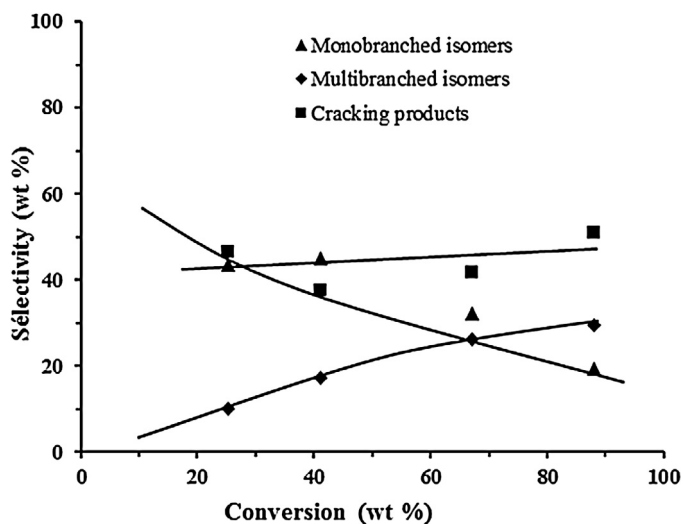


Fig. 2. Transformation of *n*-hexadecane. Selectivities towards monobranched, multibranched isomers and cracking products as function of conversion ($P = 5$ MPa, $T = 608$ K, $H_2/\text{feed} = 13$ mol/mol, Pt/silicated alumina).

The loss of activity (A/A_0) of the catalyst due to the presence of oxygenates was calculated by the ratio between the activity (A) of the catalyst for the *n*-hexadecane conversion in the presence of oxygenated molecules and the activity of the catalyst for pure *n*-hexadecane conversion (A_0).

The activity was calculated as follows (C: conversion of *n*-C₁₆):

$$A(g_{n-C_{16}} h^{-1} g_{\text{catalyst}}^{-1}) = \ln \left(\frac{100}{100 - C} \right) \times WHSV$$

When the transformation of oxygenated compounds alone was studied, conversions of decanoic acid (Conv) and of CO or CO₂ were calculated as reported below:

$$\text{Conv}_{\text{acid}}(\text{wt}\%) = \left(\frac{\sum_{n=8}^{10} A_{\text{C}_n}}{A_{\text{acid}} + \sum_{n=8}^{10} A_{\text{C}_n}} \right) \times 100$$

Table 3

Decanoic acid transformation. Calculated thermodynamic values (ΔH , ΔG , K) of the main reactions (decarbonylation, decarboxylation, hydrogenation, methanisation and Water Gas Shift) ($T = 608$ K, $P = 5$ MPa).

Reaction	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	K
Decarboxylation $C_9H_{19}COOH_{(g)} \rightarrow C_9H_{20(g)} + CO_{2(g)}$	57	-109	2.6×10^9
Decarbonylation $C_9H_{19}COOH_{(g)} + H_{2(g)} \rightarrow C_9H_{20(g)} + CO_{(g)} + H_2O_{(g)}$	96	-94	1.1×10^8
Hydrogenation $C_9H_{19}COOH_{(g)} + 2H_{2(g)} \rightarrow C_{10}H_{22(g)} + 2H_2O_{(g)}$	-62	-102	5.7×10^8
Methanization I $CO_{(g)} + H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$	-39	-16	2.6×10^1
Methanization II $CO_{2(g)} + 4H_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2O_{(g)}$	-179	-54	4.4×10^4
Water-gas shift $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$	-217	-70	1.1×10^6

Table 4

Decanoic acid transformation. Initial partial pressures of $C_9H_{19}COOH$, H_2 , H_2O , CO , CO_2 and CH_4 and calculated thermodynamic equilibrium composition ($T = 608$ K, $P = 5$ MPa).

Reaction	Compounds	Initial composition (MPa)	Equilibrium composition (MPa)
Decarbonylation	H_2	4.64	4.61
	$C_9H_{19}COOH$	0.01	5.7×10^{-15}
	C_9H_{20}	0	0.01
	H_2O	0	0.01
	CO	0	0.01
Decarboxylation	H_2	4.64	4.64
	$C_9H_{19}COOH$	0.01	1.10×10^{-37}
	C_9H_{20}	0	0.01
	CO_2	0	0.01
	H_2O	0	0.02
Hydrogenation	H_2	4.64	4.61
	$C_9H_{19}COOH$	0.01	1×10^{-37}
	$C_{10}H_{22}$	0	0.01
	H_2O	0	0.02
	CO_2	0	0.01

Table 5

Initial partial pressures of H_2 , H_2O , CO , CO_2 and CH_4 and calculated thermodynamic equilibrium composition ($T = 608$ K, $P = 5$ MPa).

Compounds	Initial composition (MPa)	Equilibrium composition (MPa)	Initial composition (MPa)	Equilibrium composition (MPa)
H_2	4.64	4.61	4.64	4.6
CO	0.01	4×10^{-11}	0	4×10^{-11}
CO_2	0	4.4×10^{-12}	0.01	4.3×10^{-12}
CH_4	0	0.01	0	0.01
H_2O	0.01	0.02	0	0.02

where A_{Cn} is the percent area for all hydrocarbons with n carbon atoms and A_{acid} is the percent area of decanoic acid.

$$Conv_{COorCO_2}(wt\%) = \frac{(m_{COorCO_2})_S}{(m_{COorCO_2})_E} \times 100$$

where $(m_{COorCO_2})_S$ is the weight of CO or CO_2 quantified at the outlet of the reactor and $(m_{COorCO_2})_E$ the weight of CO or CO_2 injected.

2.5. Catalysts characterization

The change of the Brønsted acidity, the particles size and the dispersion of platinum for spent catalysts were respectively measured by lutidine (2,6-dimethylpyridine) adsorption followed by FTIR spectroscopy and by Transmission Electron Microscopy (TEM). The amount of the acid sites was obtained from the integration of the adsorption bands at about 1629 plus 1947 cm^{-1} [23,24]. Infrared spectra were recorded with a Nicolet Magna 550 FTIR spectrometer at a resolution of 4 cm^{-1} and collected 128 scans per spectrum. Catalyst samples were pressed into thin wafers (10–20 mg for each sample) under a pressure of 0.5 $t\text{ cm}^{-2}$ and activated *in situ*, during 15 h at atmospheric pressure under a hydrogen flow (60 $cm^3\text{ min}^{-1}$) at 723 K, and then followed by 1 h of vacuum (13.3 Pa) at 673 K. After cooling down the samples until

room temperature, they were degassed under a secondary vacuum (0.002 Pa) to collect a background spectrum. Lutidine was adsorbed at ambient temperature (2 Pa) and left to equilibrate for 10 min, then the excess of physisorbed lutidine was evacuated (spectrum at room temperature, $t = 0'$). IR spectra were recorded every hour during the thermodesorption of lutidine from room temperature to 723 K by steps of 50 K. The concentration of different acid sites was calculated by using the Lambert-Beer law ($C = ((A/\epsilon) \times (S/M)) \times 1000$), where C is the concentration of acid sites ($\mu\text{mol g}^{-1}$), A the area of the peak, S the surface of the wafer (2 cm^2), ϵ the molar extinction coefficient (1.13 $cm\text{ }\mu\text{mol}^{-1}$) and finally m the mass of the sample [25]. All the spectra were normalized to an equivalent sample mass of 10 mg. The particles size of platinum was measured by Transmission Electron Microscopy (TEM) using a Philips CM 120 microscope (120 kV) equipped with a LaB₆ filament. The mean particle size and size distribution were determined by measuring the diameter of isolated particles using the ImageJ software [26]. The dispersion (D) was calculated using the following equation: $D(\%) = (6/(\rho_{Pt} \times S_{Pt} \times d(m))) \times 100$ with S_{Pt} the specific surface area (275 $m^2\text{ g}^{-1}$), ρ_{Pt} the density of the platinum (21.45106 $g\text{ cm}^{-3}$) and $d(m)$ the average of particle size.

The spent catalysts were characterized by elemental analysis (CE Instruments NA2100 Protein) in order to measure the carbon amount after washing with CH_2Cl_2 .

3. Results

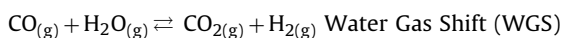
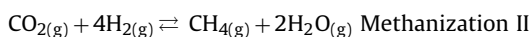
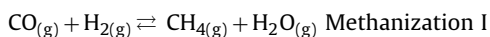
3.1. Thermodynamic calculations

From the thermodynamic point of view, the transformation of decanoic acid was investigated under the operating conditions of the transformation of *n*-hexadecane.

The transformation of the decanoic acid could involve various reactions (Table 3):

1. decarbonylation reaction leading to the formation of nonane and CO,
2. decarboxylation reaction also leading to the formation of nonane and CO₂,
3. hydrogenation reaction leading to the formation of decane and water.

Moreover, under these operating conditions, CO can be converted into methane via methanization reaction or CO₂ via the water-gas shift reaction. CO₂ can also be methanized.



Enthalpy of reaction (ΔH), free enthalpy (ΔG) and the equilibrium constant (K) for the different reactions were calculated at 608 K (Table 3). At this temperature, the reaction enthalpy (ΔH) is negative for the hydrogenation reaction of decanoic acid, for both reactions of methanization and water-gas shift reaction. This indicates that the reactions are exothermic. However, the reaction enthalpy (ΔH) is positive for the decarboxylation and decarbonylation reactions indicating that these reactions are endothermic. All reactions are spontaneous at this temperature ($\Delta G < 0$) and the equilibrium constants are much greater than 1. The composition at equilibrium from decanoic acid and from its transformation products (H₂O, CO and CO₂) was determined under the operating conditions considering an initial partial pressure of 0.1 bar and decarbonylation, decarboxylation and hydrogenation reactions. This corresponds to the maximum content of acid injected in the presence of *n*-hexadecane. It can be seen, Table 4, that from a thermodynamic point of view, decanoic acid can be completely converted into hydrocarbons (nonane or decane) and CO or CO₂ or H₂O by the proposed reactions. In addition, CO and CO₂ can also be totally methanized under the chosen operating conditions (Table 5).

3.2. Catalytic measurements

3.2.1. Hydroconversion of pure *n*-hexadecane

The change of the conversion (C) of the *n*-hexadecane and the selectivity towards isomerization (S_{isom}) and cracking (S_{cr}) over Pt/silicated alumina catalyst as function of the residence time ($1/\text{WHSV}$) are reported Fig. 1. An increase of the conversion with the residence time was noticed corresponding to a pseudo first kinetic order regarding the reactant. In the range of residence time studied (corresponding to conversions varying from 20 to 90%), the selectivities towards global isomerization (corresponding to the sum of monobranched and multibranched products) and cracking were rather stable, the isomerization being slightly (55%) favored up to 70% conversion. The monobranched isomers appeared as primary products and their selectivity decreased with the conversion (Fig. 2). On the contrary, the selectivity towards multibranched isomers increased with conversions until 80% and then decreased.

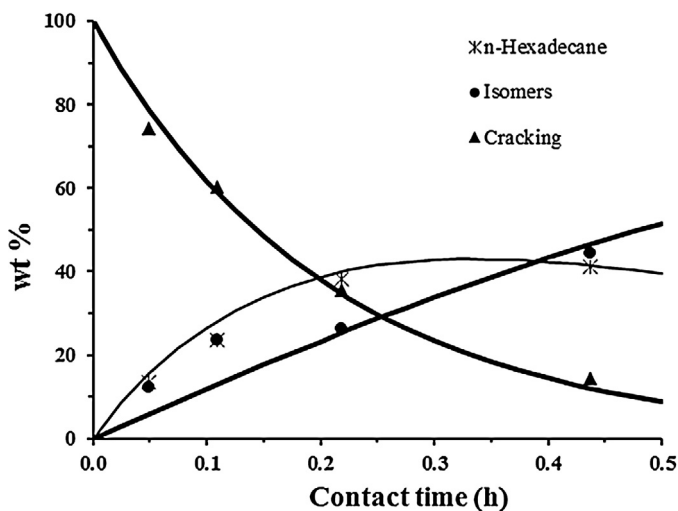


Fig. 3. Comparison of theoretical curves (solid lines) and experimental data (symbols) of disappearance of *n*-hexadecane and formation of isomerization and cracking products ($P = 5$ MPa, $T = 608$ K, $\text{H}_2/\text{feed} = 13$ mol/mol, Pt/silicated alumina).

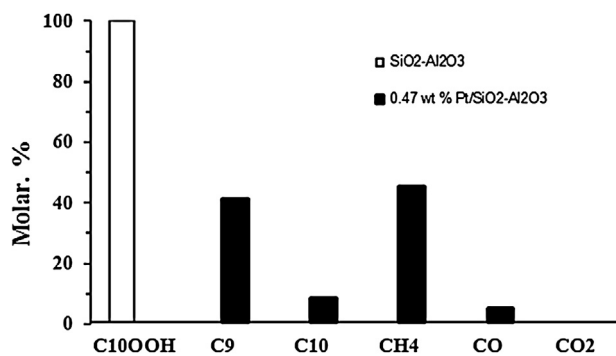


Fig. 4. Transformation of decanoic acid over Pt/silicated alumina and silicated alumina. Hydrocarbon product molar distribution ($P = 5$ MPa, $T = 608$ K, $1/\text{WHSV} = 0.058$ h, $\text{H}_2/\text{feed} = 13$ mol/mol).

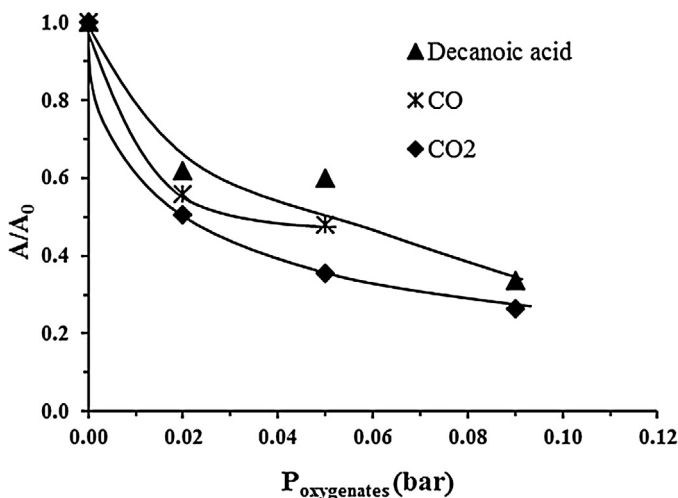


Fig. 5. Transformation of *n*-hexadecane – Impact of oxygenates (decanoic acid, CO and CO₂) (Step B). Loss of activity (A/A_0) as function of oxygenates partial pressure ($P = 5$ MPa, $T = 608$ K, $\text{H}_2/\text{feed} = 13$ mol/mol, Pt/silicated alumina).

Finally selectivity towards cracking products remained constant in a range of conversions from 20 to 80%. Rate constants of isomerization and cracking were calculated considering the Scheme 2 and using the Deplot [27] method as previously reported by Girgis and

Tsao [28] and Calemme et al. [29] to determine the reaction mechanism of hydrocracking and hydroisomerization of *n*-hexadecane on bifunctional catalysts based on platinum on silicated alumina. Indeed, from the product selectivity curves as function of the conversion of the reactant, it allows the discrimination between primary products (formed directly from *n*-hexadecane) and those corresponding to secondary products or higher ranks (formed by successive reactions of intermediates). The different rate equations corresponding to the disappearance of *n*-hexadecane (A) and the formation of isomerization products (B) and cracking (C) were developed assuming a plug flow reactor, the absence of diffusional limitations and considering a quasi-stationary state.

$$-\frac{d[A]}{dt} = (k_1 + k_3)[A] \quad (1)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \quad (2)$$

$$\frac{d[C]}{dt} = k_3[A] + k_2[B] \quad (3)$$

The concentration of each compound (A, B, C) as function of residence time is determined from the following equations

$$[A]_t = A_0 e^{-(k_1 + k_3)t} \quad (4)$$

$$[B]_t = \frac{A_0 k_1}{k_2 - k_1 - k_3} (e^{-(k_1 + k_3)t} - e^{-k_2 t}) \quad (5)$$

Table 6

Transformation of *n*-hexadecane. Calculated kinetic constants (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

k_1 (h ⁻¹)	k_2 (h ⁻¹)	k_3 (h ⁻¹)
2.955	1.676	0.541

$$[C]_t = A_0 \left(1 + \frac{k_1 e^{-k_2 t} - (k_2 - k_3) e^{-(k_1 + k_3)t}}{k_2 - k_1 - k_3} \right) \quad (6)$$

With k_1 , k_2 and k_3 rate constants of the formation respectively of isomerization products (corresponding to sum of mono-branched and multi-branched products) from the *n*-hexadecane, cracking products from the isomerization products and from *n*-hexadecane. A good correlation between experimental and calculated values is obtained as shown Fig. 3 where the disappearance of *n*-hexadecane, the formation of isomerization products and cracking products are reported as function of residence time. The rate constants calculated and used to obtain the curves are summarized Table 6. These values correctly reflect the results. Indeed, it is observed a k_1 rate constant higher than k_2 and k_3 corresponding to greater selectivity towards isomerization than selectivity towards cracking products obtained from direct or secondary cracking from *n*-hexadecane. Moreover, these results confirm the experimental observations where the isomerization products are primary products. Similarly, the cracking products may also come directly from the *n*-hexadecane and from isomerization products. This also validates the apparent reaction scheme for the conversion

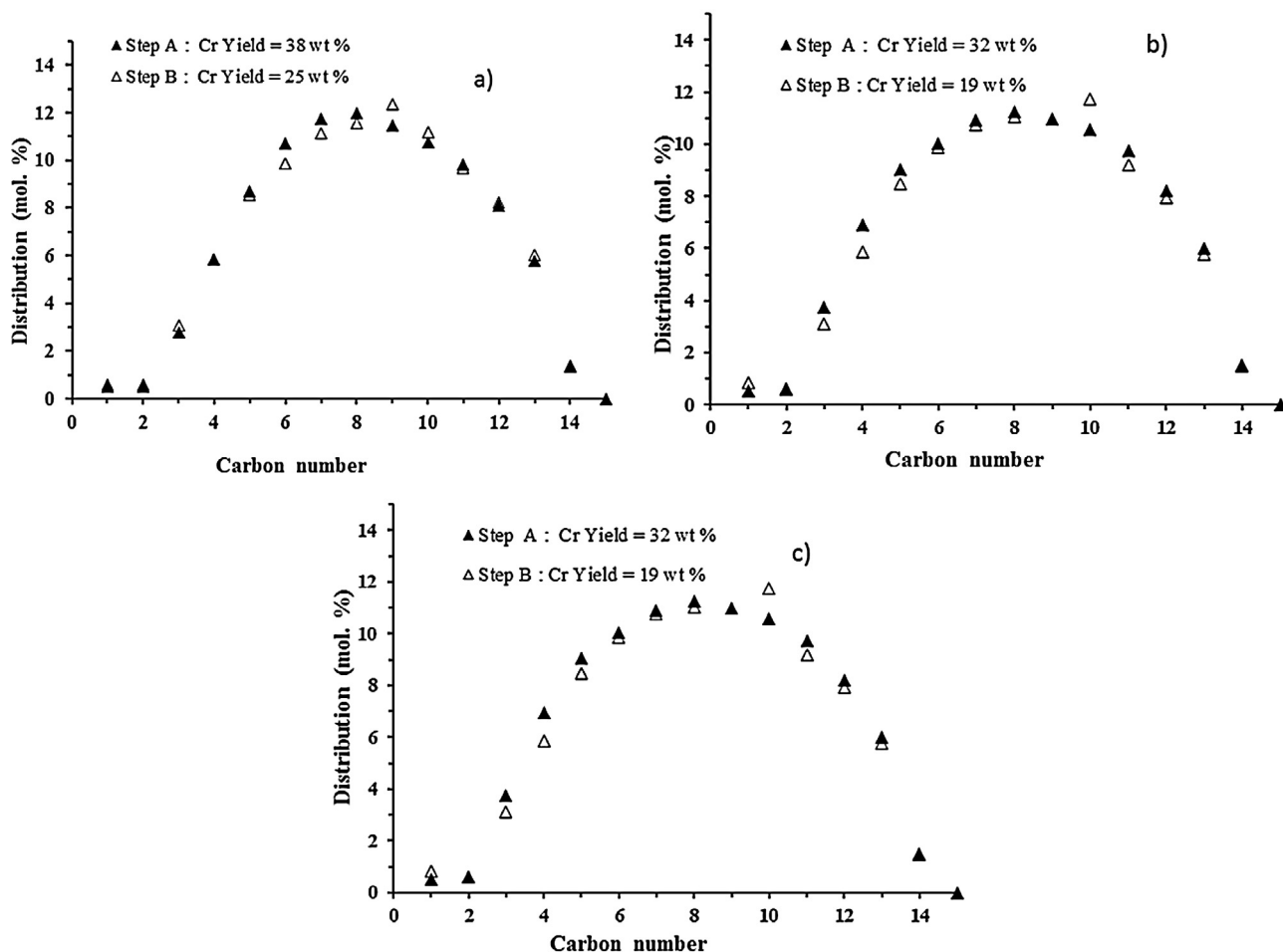


Fig. 6. Transformation of *n*-hexadecane. Impact of (a) 2, (b) 5 and (c) 9 kPa of decanoic acid. Molar distribution products of cracked products for step A and B of the experimental procedure (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

of *n*-hexadecane (Scheme 2), under these operating conditions, where all the isomers (mono-branched and multi-branched) were lumped.

3.2.2. Transformation of decanoic acid and its by products under hydrocracking conditions

Under the selected operating conditions, the decanoic acid was not transformed on the silicated alumina support and the conversion was complete ($1/\text{WHSV}=0.058\text{ h}$) over the bifunctional catalyst (Fig. 4). Nonane, methane, decane and carbon monoxide were observed as reaction products. This involved mainly decarbonylation and decarboxylation reactions corresponding to the formation of nonane (accounting for 41 mol% of the reaction products). However, it is not possible to differentiate these two reactions because they lead to the same product (nonane) and CO and CO_2 formed were almost totally methanized. Indeed, the amount of methane and nonane produced are very similar. Decanoic acid was also converted via the hydrogenation reaction as decane was observed in the reaction products (9 mol%). Based on the relative amounts of nonane and decane produced, around 80% of the decanoic acid is converted by the decarboxylation/decarbonylation pathway, and 20% by the hydrogenation pathway.

Under the same operating conditions, CO or CO_2 alone (using a range of partial pressures of CO and CO_2 from 2 to 9 kPa corresponding to those generated from the transformation of decanoic acid alone) are completely converted over the catalyst into methane and water. Furthermore, the water formed during these experiments cannot be quantified.

3.2.3. Impact of oxygenated compounds on the hydroconversion of *n*-hexadecane

***N*-Hexadecane hydroconversion with oxygenates cofeeding.** The impact of decanoic acid, CO or CO_2 (by-products of the transformation of decanoic acid) on the catalyst activity for *n*-hexadecane conversion is reported Fig. 5. Under these experimental conditions, decanoic acid, CO or CO_2 are completely converted for all partial pressures studied. A negative and significant effect when small amounts of oxygenates (2 kPa) were introduced in the feed was observed. The loss of catalyst activity is represented by the (A/A_0) ratio between activity in the presence of oxygenated molecule (A) and the absence of oxygenated molecule (A_0). For example, in the presence of decanoic acid, a loss of activity of 26% for a partial pressure of 2 kPa and 65% for a partial pressure of 9 kPa of acid (2 wt%) was observed. This result (Table 7) corresponds also to an evolution in isomerization (mono-branched and multi-branched) and cracking products selectivities and methane yield. The selectivity

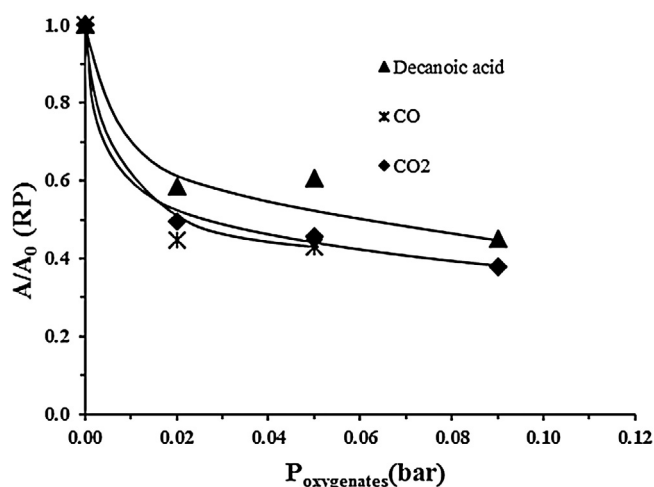


Fig. 7. Transformation of *n*-hexadecane—impact of oxygenates. Loss of activity (A/A_0 (RP)) (step C of the procedure) as function of the partial pressure of oxygenates (Pt/silicated alumina, $P=5\text{ MPa}$, $T=608\text{ K}$, $\text{H}_2/\text{feed}=13\text{ mol/mol}$).

towards isomerisation increases from 55 to 71% corresponding to a decrease of the selectivity towards cracking after an increase of the partial pressure of decanoic acid from 0 to 9 kPa. The selectivity towards mono-branched isomers increases from 31 to 51% for the maximum acid content. In contrast, the multi-branched isomers selectivity (about 20–22%) remains stable when the amount of acid increases. The methane yield decreases (CH_4 Yield-total) from 0.16 to 0.11% by the introduction of the lower acid content. However, when the partial pressure of acid added increases from 2 to 9 kPa, the yield of CH_4 increases from 0.11 to 0.15%. This is explained by the formation of methane in one hand from the hydrocarbons by hydrogenolysis over platinum and on the other hand from the decomposition of the acid by the decarbonylation and decarboxylation reactions followed by methanization of CO and CO_2 produced. This is in accordance with the results of the transformation of the CO and CO_2 studied alone. It is then possible to estimate the amount of methane produced by the decomposition of the acid through the formation of nonane by the decarbonylation and decarboxylation reactions followed by methanization of CO and CO_2 produced. Therefore, the difference between the total amount of methane analyzed and calculated by the decomposition of the acid allows access to methane formation due to hydrogenolysis reaction on the metal (CH_4 Yield-Metal). The methane yield (CH_4 Yield-Metal)

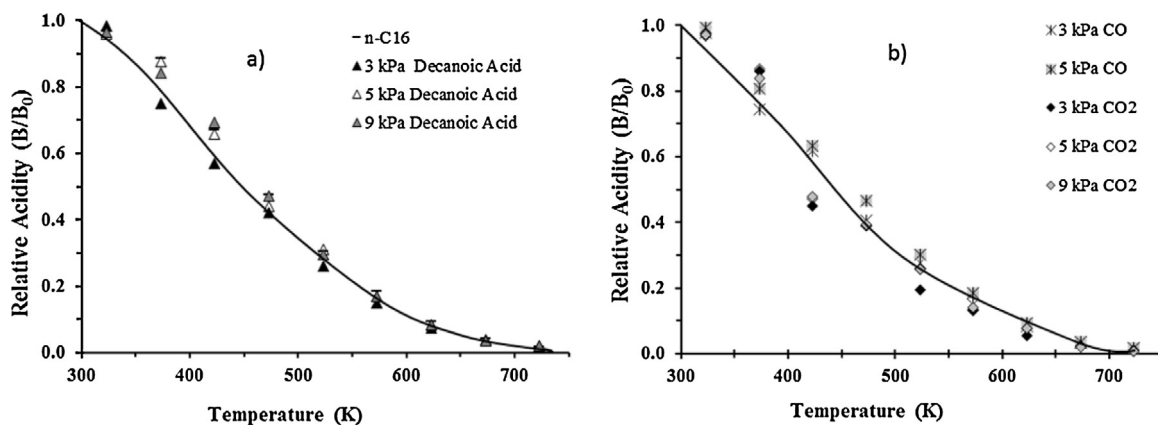


Fig. 8. Evolution of the relative acidity measured by the B/B_0 ratio (B_0 : total Brønsted acidity measured by Lutidine adsorption at room temperature, B : Brønsted acidity at a temperature) as function of temperature for the Pt/silicated alumina catalyst after the conversion of *n*-hexadecane in the presence of various amount of (a) decanoic acid (b) CO or CO_2 .

Table 7Transformation of *n*-hexadecane during cofeeding with various amount of decanoic acid (Step B).

Decanoic acid (kPa)	C. (wt.%)	A/A ₀	S _{Isom} (wt.%)	S _{Mono} (wt.%)	S _{Multi} (wt.%)	S _{Cr} (wt.%)	Y _{T-CH₄} (wt.%)	Y _{M-CH₄} (wt.%)
0	72	1	55	31	25	44	0.16	0.16
2	61	0.74	59	39	20	41	0.11	0.09
5	53	0.59	64	42	22	36	0.12	0.08
9	36	0.35	71	51	20	29	0.15	0.02

Conversion (C.), loss of activity (A/A₀) and selectivities towards isomerization (S_{Isom}, S_{Mono} and S_{Multi}) and cracking (S_{Cr}) as a function of the amount of decanoic acid. (C.: *n*-hexadecane conversion, A: activity of the catalyst for *n*-hexadecane conversion in the presence of various amount of decanoic acid, A₀: initial activity of the catalyst for *n*-hexadecane conversion in the absence of oxygenates, S_{Isom}: selectivity towards isomerization, S_{Mono}: selectivity towards monobranched products, S_{Multi}: selectivity towards multibranched products and S_{Cr}: selectivity towards cracked products, Y_{T-CH₄}: total yield of methane, Y_{M-CH₄}: yield of methane from hydrogenolysis) (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

due to hydrogenolysis on platinum decreases from 0.16 to 0.02% when the partial pressure of acid increases from 2 to 9 kPa.

The distribution of cracked products is not affected (Fig. 6a–c) respectively in the presence of 2, 5 and 9 kPa of acid. Indeed, one always observes a symmetrical distribution centered on C₈ demonstrating the absence of over-cracking. These results are shown for cracking yields of 38, 32 and 33% without acid and respectively 25, 19, and 11% in the presence of decanoic acid. The points corresponding to C₉ and C₁₀ compounds are outside the distribution of hydrocracking products of *n*-hexadecane. This corresponds to the complete conversion of the acid. One can also see that the decarbonylation and decarboxylation reactions (Fig. 6c) predominate in relation to the hydrogenation pathway (cf. nonane formation relative to decane). This is in perfect agreement with the results observed for the transformation of decanoic acid alone.

CO and CO₂ also have a significant negative impact on the catalyst activity for the transformation of *n*-hexadecane (Fig. 5). This effect is similar for the addition of small amounts of CO or CO₂ (2 kPa). Under these conditions, both compounds are totally methanized which corresponds to an increase of the CH₄ content. Thus, a loss of activity of about 35 and 52% (corresponding to A/A₀ ratios of 0.65 and 0.48) was observed for CO partial pressure of 2 kPa and 5 kPa respectively (Table 8). The loss of activity is about 50 and 74% (corresponding to A/A₀ ratios of 0.50 and 0.26) for CO₂ partial pressure of 2 kPa and 9 kPa respectively.

As observed for decanoic acid, cofeeding hexadecane with CO or CO₂ induces a modification of selectivities towards isomerization and cracking, in favour of isomerization (see Table 8 and 9 respectively for CO and CO₂). Methane yields produced by hydrogenolysis decrease in the presence of CO or CO₂ as already observed for

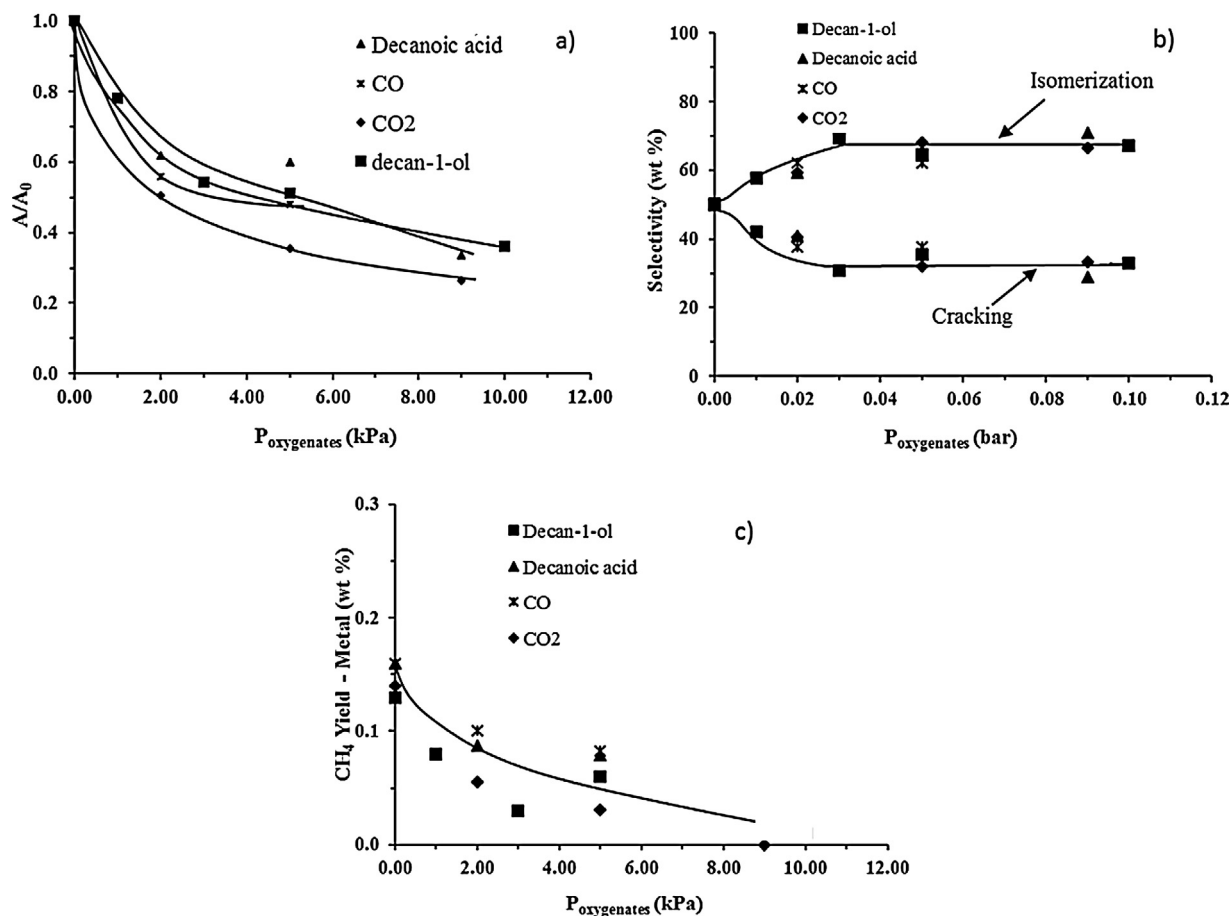


Fig. 9. Transformation of *n*-hexadecane—impact of decan-1-ol (■), decanoic acid (▲), CO (×) and CO₂ (◆). Evolution of (a) loss of activity, (b) selectivities and (c) methane produced by hydrogenolysis (CH₄-Yield-Metal) as function of the partial pressure of oxygenates (step B). (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

Table 8Transformation of *n*-hexadecane during cofeeding with various amount of CO (Step B).

P _{CO} (kPa)	C. (wt.%)	A/A ₀	S _{Isom} (wt.%)	S _{Mono} (wt.%)	S _{Multi} (wt.%)	S _{Cr} (wt.%)	Y _{T-CH₄} (wt.%)	Y _{M-CH₄} (wt.%)
0	72	1	56	31	25	44	0.16	0.16
2	56	0.65	62	41	21	38	0.13	0.10
5	46	0.48	65	44	18	38	0.18	0.08

Conversion (C.), loss of activity (A/A₀) and selectivities towards isomerization (S_{Isom}, S_{Mono} and S_{Multi}) and cracking (S_{Cr}) as a function of the amount of CO. (C.: *n*-hexadecane conversion, A: activity of the catalyst for *n*-hexadecane conversion in the presence of various amount of CO, A₀: initial Activity of the catalyst for *n*-hexadecane conversion in the absence of oxygenates, S_{Isom}: selectivity towards isomerization, S_{Mono}: selectivity towards monobranched products, S_{Multi}: selectivity towards multibranched products and S_{Cr}: selectivity towards cracked products, Y_{T-CH₄}: total yield of methane, Y_{M-CH₄}: yield of methane from hydrogenolysis (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

Table 9Conversion of *n*-hexadecane during cofeeding with various amount of CO₂ (Step B).

P _{CO₂} (kPa)	C. (wt.%)	A/A ₀	S _{Isom} (wt.%)	S _{Mono} (wt.%)	S _{Multi} (wt.%)	S _{Cr} (wt.%)	Y _{T-CH₄} (wt.%)	Y _{M-CH₄} (wt.%)
0	72	1	55	32	23	45	0.16	0.16
2	47	0.50	59	42	17	41	0.09	0.06
5	34	0.33	68	51	17	32	0.12	0.03
9	28	0.26	66	53	13	34	0.15	0.00

Conversion (C.), loss of activity (A/A₀) and selectivities towards isomerization (S_{Isom}, S_{Mono} and S_{Multi}) and cracking (S_{Cr}) as a function of the amount of CO. (C.: *n*-hexadecane conversion, A: activity of the catalyst for *n*-hexadecane conversion in the presence of various amount of CO₂, A₀: initial activity of the catalyst for *n*-hexadecane conversion in the absence of oxygenate, S_{Isom}: selectivity towards isomerization, S_{Mono}: selectivity towards monobranched products, S_{Multi}: selectivity towards multibranched products and S_{Cr}: selectivity towards cracked products), Y_{T-CH₄}: total yield of methane, Y_{M-CH₄}: yield of methane from hydrogenolysis (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

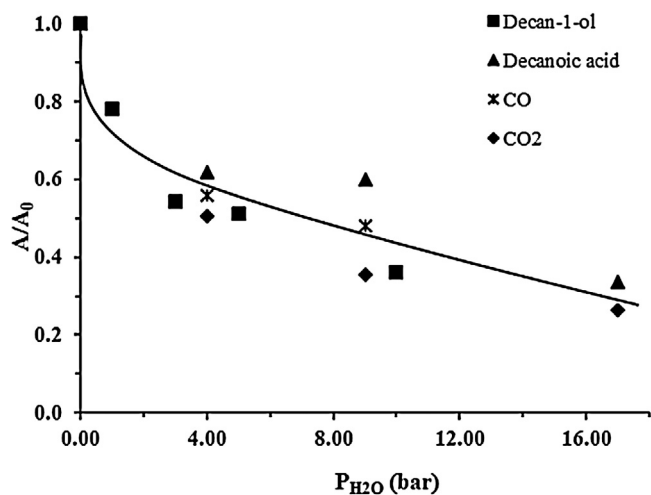


Fig. 10. Transformation of *n*-hexadecane—impact of decan-1-ol (■), decanoic acid (▲), CO (×) and CO₂ (◆). Evolution of the loss of activity as function of the partial pressure of water produced (step B) (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

decanoic acid. The distribution of cracked products (not reported) is not affected by the addition of 2 and 5 kPa of CO or CO₂.

***N*-Hexadecane hydroconversion after oxygenates cofeeding.**

After stopping the introduction of the oxygenates (decanoic, CO or CO₂, step C of the procedure), the catalyst activity for the transformation of *n*-hexadecane is not recovered. It decreases with the increase of the partial pressure of the oxygenates (decanoic acid, CO or CO₂) introduced (Fig. 7). For example, a loss of activity (A/A₀ (RP: return point)) of almost 54% was observed after the introduction of 9 kPa of decanoic acid. This corresponds also to a modification of the selectivities towards isomerization and cracking products. Indeed an increase of the selectivity towards isomerization corresponding to the decrease of the selectivity towards cracking products was noticed (Table 10–12 respectively for decanoic acid, CO and CO₂). The selectivities were then stabilized for higher amount of oxygenates. In the same way, the methane yield was not also recovered after stopping the introduction of oxygenates which confirms the irreversible modification of the hydrogenolysis activity of platinum.

On the contrary, no modification of the distribution of cracked products (not reported here) according to carbon chain length is observed.

3.2.4. Impact of oxygenated compounds on the catalyst physicochemical properties

Table 13 reports the amount of carbon, platinum particle size and Brønsted acidity for the spent catalysts unloaded after each catalytic test. Residual carbon content is low and similar for all catalysts. An increase of platinum particle size of 1.2–1.8 nm is evidenced with increasing partial pressure of the oxygenated molecules during the test, regardless of the kind of oxygenate. This also corresponds to a decrease of the platinum dispersion which corresponds to a sintering of the platinum. Finally, all the catalyst exposed to oxygenates exhibited a lower total Brønsted acidity compared to the catalyst exposed to *n*-hexadecane only. In contrast, exposition of the catalyst to oxygenate has no impact on the Brønsted acid sites distribution as reported Fig. 8a and b respectively.

4. Discussion

N-Hexadecane, in agreement with the literature [24,30,29], is transformed over Pt/silicated alumina catalyst according to a conventional hydrocracking apparent scheme where the mono-branched products appear as primary products, the multi-branched products as secondary products and cracking products can appear as primary and/or subsequent to the isomerization (Scheme 2). The overall rate constants for each step were determined and the theoretical curves obtained using these values have allowed to report correctly the experimental results. This behavior is not typical of an ideal hydrocracking catalyst where the *n*-alkane is transformed successively into monobranched isomers, multibranched isomers and cracked products, as already discussed in [22]. Decanoic acid is totally converted under hydrocracking conditions only on the metallic function and not on the acidic function of the catalyst. The decanoic acid is transformed over platinum via decarboxylation reactions (leading to nonane and CO₂ formation), decarbonylation (corresponding to nonane and CO formation) and hydrogenation (leading to decane and water, Scheme 3). Reactions of decarboxylation and decarbonylation are favored since the formation of

Table 10Transformation of pure *n*-hexadecane (step C) after cofeeding with various amount of decanoic acid.

Decanoic acid (kPa)	C. (wt.%)	A/A ₀	S _{Isom} (wt.%)	S _{Mono} (wt.%)	S _{Multi} (wt.%)	S _{Cr} (wt.%)	Y _{T-CH₄} (wt.%)
0	72	1	55	31	25	44	0.16
2	60	0.72	62	38	22	38	0.07
5	55	0.63	69	43	26	31	0.15
9	44	0.46	84	48	36	16	0.03

Conversion (C.), loss of activity (A/A₀) and selectivities towards isomerization (S_{Isom}, S_{Mono} and S_{Multi}) and cracking (S_{Cr}) (C.: *n*-hexadecane conversion, A: activity of *n*-hexadecane in the presence of various amount of decanoic acid, A₀: initial activity of *n*-hexadecane alone, S_{Isom}: selectivity towards isomerization, S_{Mono}: selectivity towards monobranched products, S_{Multi}: selectivity towards multibranched products and S_{Cr}: selectivity towards cracked products, Y_{T-CH₄}: total yield of methane) (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

Table 11Transformation of pure *n*-hexadecane (step C) after cofeeding with various amount of CO.

P _{CO} (kPa)	C. (wt.%)	A/A ₀	S _{Isom} (wt.%)	S _{Mono} (wt.%)	S _{Multi} (wt.%)	S _{Cr} (wt.%)	Y _{T-CH₄} (wt.%)
0	72	1	56	31	25	44	0.16
2	48	0.51	74	51	23	26	0.05
5	43	0.44	73	56	21	28	0.05

Conversion (C.), loss of activity (A/A₀) and selectivities towards isomerization (S_{Isom}, S_{Mono} and S_{Multi}) and cracking (S_{Cr}) (C.: *n*-hexadecane conversion, A: activity of *n*-hexadecane in the presence of various amount of CO, A₀: initial activity of *n*-hexadecane alone, S_{Isom}: selectivity towards isomerization, S_{Mono}: selectivity towards monobranched products, S_{Multi}: selectivity towards multibranched products and S_{Cr}: selectivity towards cracked products, Y_{T-CH₄}: total yield of methane) (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

Table 12Conversion of pure *n*-hexadecane (step C) after cofeeding with various amount of CO₂.

P _{CO₂} (kPa)	C. (wt.%)	A/A ₀	S _{Isom} (wt.%)	S _{Mono} (wt.%)	S _{Multi} (wt.%)	S _{Cr} (wt.%)	Y _{T-CH₄} (wt.%)
0	71	1	55	32	23	45	0.14
0.02	46	0.46	73	51	22	27	0.03
0.05	41	0.41	78	56	22	22	0.02
0.09	38	0.38	80	58	22	20	0.02

Conversion (C.), loss of activity (A/A₀) and selectivities towards isomerization (S_{Isom}, S_{Mono} and S_{Multi}) and cracking (S_{Cr}) (C.: *n*-hexadecane conversion, A: activity of *n*-hexadecane in the presence of various amount of CO₂, A₀: initial activity of *n*-hexadecane alone, S_{Isom}: selectivity towards isomerization, S_{Mono}: selectivity towards monobranched products, S_{Multi}: selectivity towards multibranched products and S_{Cr}: selectivity towards cracked products, Y_{T-CH₄}: total yield of methane) (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

Table 13Catalyst characterization—impact of oxygenates (partial pressure of oxygenates: P_{ox}), particles size, dispersion, carbon amount and total amount of adsorbed lutidine of various spent catalyst.

Oxygenates	P _{ox} (kPa)	Platinum particles size (nm)	Platinum dispersion (%)	Carbon (%pds)	Total amount of adsorbed lutidine (μmol g ⁻¹)
Decanoic acid	0	1.2	85	0.4	197
	2	1.3	78	0.6	135
	5	1.5	68	0.6	151
	9	1.8	54	0.7	146
CO	2	1.2	85	0.3	183
	5	1.3	78	0.4	168
CO ₂	2	1.2	85	0.3	120
	5	1.2	85	0.3	153
	9	1.4	73	0.6	146

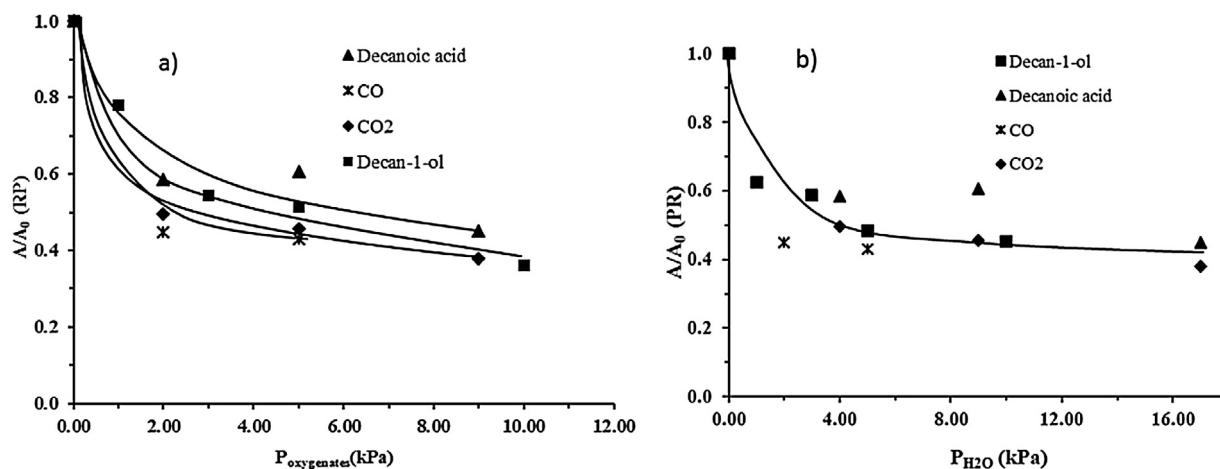


Fig. 11. Transformation of *n*-hexadecane —impact of decan-1-ol (■), decanoic acid (▲), CO (×) and CO₂ (◆). Evolution of the loss of activity A/A₀ (RP) after stopping the introduction of the oxygenated molecule (step C) as function of (a) partial pressure of oxygenates and (b) partial pressure of water produced (P = 5 MPa, T = 608 K, H₂/feed = 13 mol/mol, Pt/silicated alumina).

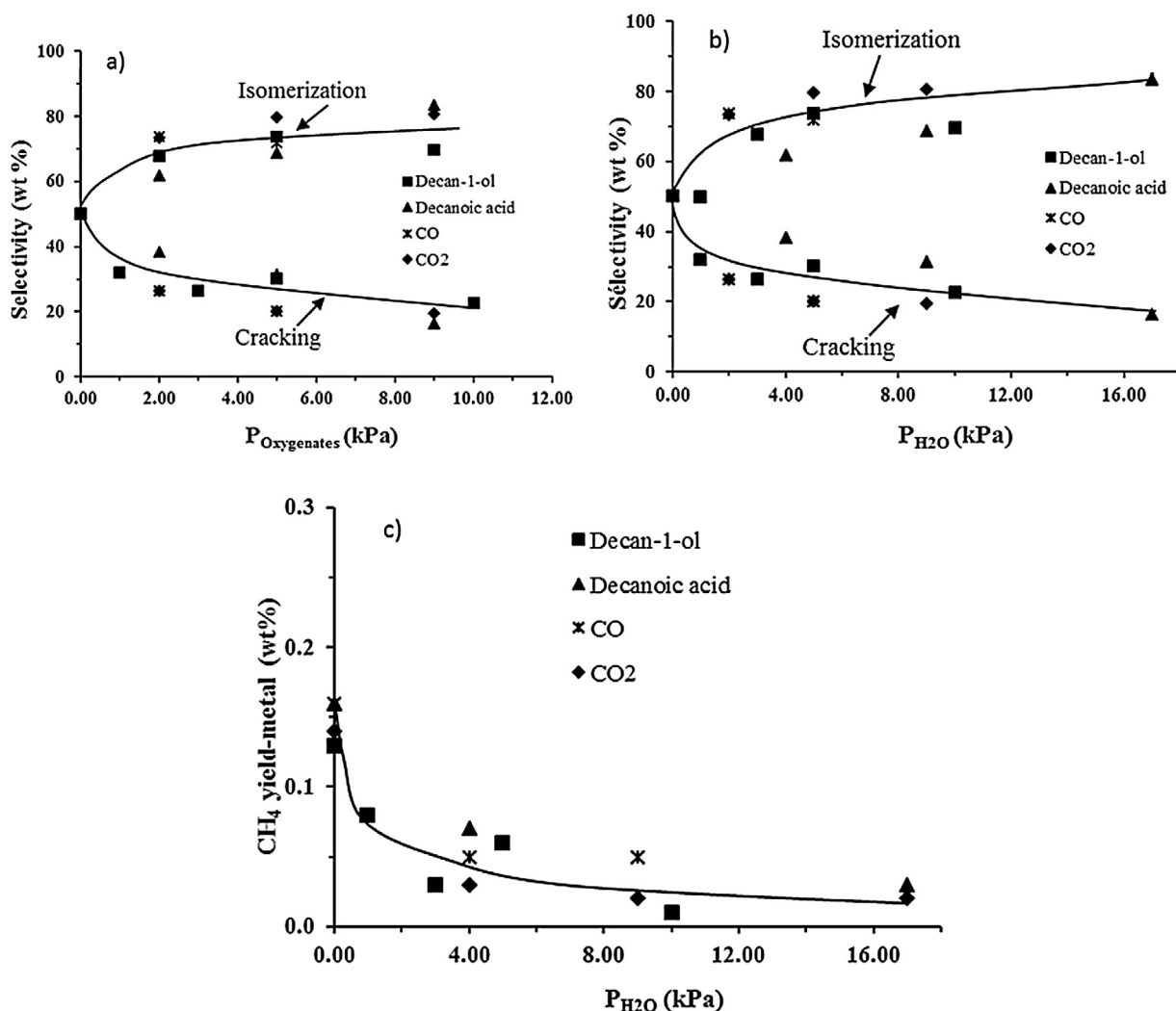


Fig. 12. Transformation of *n*-hexadecane—impact of decan-1-ol (■), decanoic acid (▲), CO (×) and CO₂ (◆). Evolution after stopping the introduction of the oxygenated molecules (step C) of (a) selectivities as function of partial pressure of oxygenates (b) selectivities as function of partial pressure of water produced (c) yield of methane as function of water produced ($P = 5$ MPa, $T = 608$ K, $\text{H}_2/\text{feed} = 13$ mol/mol, Pt/silicated alumina).

nonane (decarbonylation and decarboxylation reactions) is higher than the formation of decane (hydrogenation reaction). Indeed around 80% of the decanoic acid is converted by the decarboxylation/decarbonylation pathway, and 20% by the hydrogenation pathway. The reaction scheme of the transformation of decanoic acid is in total agreement with the one established under different hydrotreatment operating conditions (hydrodesulfurization of gas oils and hydrodeoxygenation of liquid of biomass from pyrolysis). Indeed, the decanoic acid was mainly transformed by the decarbonylation and decarboxylation pathways over sulfided Ni(Co)Mo/Al₂O₃ [30] or CoMoP/Al₂O₃ [31] ($T = 613$ K, $P = 4$ MPa).

CO and CO₂ were totally converted into methane and water by methanization reaction. Whatever the oxygenated model molecules considered, water appears as the final oxygenated product produced over the catalyst under the operating conditions of hydrocracking. When the oxygenates (decanoic acid, CO or CO₂) were cofeeded (Step B) with *n*-hexadecane, a negative impact of oxygenates on the catalyst activity on the hydroconversion of *n*-hexadecane was clearly evidenced. This effect was found to be close for all of the model oxygen molecules studied. It could be possible also to associate results obtained previously by Guedes et al. [22] in the same operating conditions with decan-1-ol as model molecule. Indeed, the loss of activity measured by the ratio (A/A_0) between

the activity (A) for the conversion of *n*-hexadecane in the presence of oxygenated compounds and activity (A_0) for the conversion of pure *n*-hexadecane decreases sharply at low partial pressures of decanoic acid, CO and decan-1-ol (Fig. 9a). This trend then reduces for higher partial pressures. Moreover, it seems that the CO₂ is slightly more inhibiting than other oxygenates (loss of activity of about 70% instead of 60% for other oxygenates for oxygen partial pressure of 9 kPa). As reported previously for decan-1-ol [22], it could be possible to estimate the amount of platinum involved for the total transformation of the decanoic acid, CO or CO₂ taking account of the residence time and the flow of acid or CO or CO₂. The catalyst mass required for the complete conversion of the decanoic acid under these operating conditions was 0.13 g which corresponds at 10% of the total weight of catalyst. In addition, CO or CO₂ injected directly or formed during the decomposition of the acid are completely converted into methane under these operating conditions, which also leads to the formation of water. The complete conversion of CO and CO₂, requires only catalyst masses of 0.018 g and 0.011 g, respectively for CO and CO₂ (representing only 1.8 and 1.1% of the mass of catalyst). This clearly demonstrates that the real contaminant would not be the oxygenates themselves but rather water produced by their transformation which would be in contact with the majority of the catalyst unlike oxygenates.

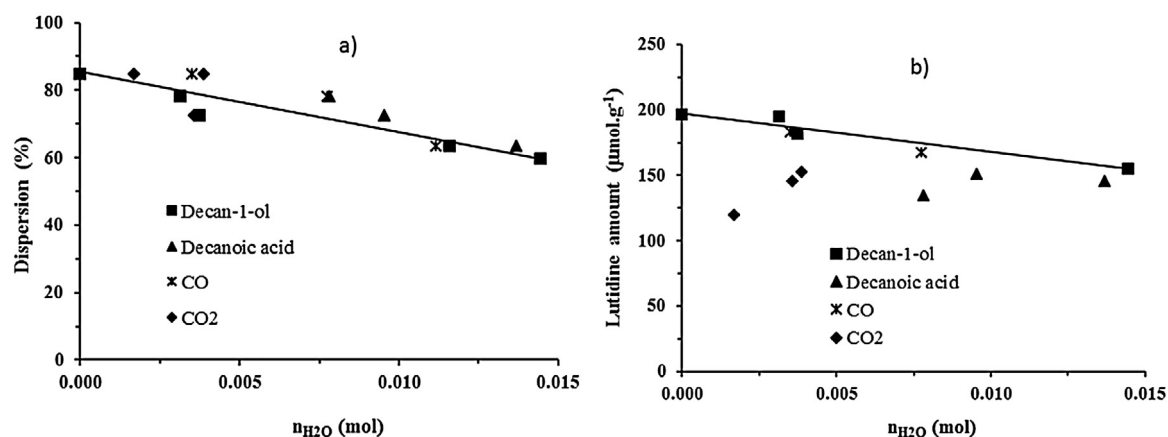


Fig. 13. Evolution of the (a) dispersion of platinum particles and (b) catalyst total Brønsted acidity as function of the amount of water produced by the transformation of decan-1-ol (■), decanoic acid (▲), CO (×), CO₂ (◆) (step B of the procedure).

The impact of oxygenates is very close regardless the nature of the molecules (acid, alcohol, CO and CO₂). Indeed, the evolution of the loss of activity (A/A_0) when the oxygenate molecules were injected simultaneously with *n*-hexadecane (step B of the procedure) as function of the partial water produced by the decomposition of the various oxygenating molecules, shows the same negative impact that from all the oxygenates (Fig. 10). Moreover, as reported previously [22], the results obtained by injecting directly water even at a much higher partial pressure (43 times), even following this trend in the presence of decan-1-ol as model molecule.

The presence of oxygenates also results in a substantial change in selectivities towards isomerization and cracking, which is also identical regarding the introduced oxygenated molecules (Fig. 9b). Thus, in the presence of a low partial pressure of oxygenates, the selectivity towards isomerization is favored and the selectivity towards cracking disfavored. Indeed, the selectivity towards isomerization increases from about 50% to about 70% by the presence of an oxygenate partial pressure of 4 kPa and is stable beyond. Simultaneously, the methane formation due to hydrogenolysis over platinum also decreases sharply (Fig. 9c). This reflects a change in the balance between hydro-dehydrogenated properties of the metal and the acid function of the support. Some works in the literature reports similar studies [32]. It is necessary to consider competitive adsorptions between oxygenates and *n*-hexadecane, oxygenates being more adsorbed. The adsorption of the acid appears to occur preferentially on the metal sites. Indeed, no transformation of the acid was noticed over the silicated alumina support alone whereas the acid was rapidly transformed over platinum/silicated alumina catalyst. These results are in accordance with the study of Leckel [5] on the effect of lauric acid on hydrocracking hydrogenated Fischer-Tropsch waxes. The presence of acid, decreasing the ratio between the available metal sites and acid sites, increases the selectivity towards naphtha and decreases the selectivity towards gas oils. Indeed, lauric acid adsorbed on the metal sites and not on the acidic support. The overall results also showed the irreversibility of the impact of oxygenates or rather water compounds on acid, hydro-dehydrogenating and purely metallic properties of the catalyst. Indeed, after stopping the injection of each of the oxygenated molecules (step C of the procedure), the catalyst activity for the conversion of *n*-hexadecane was not restored. A loss of activity (A/A_0 (RP)) of 55% after the cofeeding of alcohol or acid, 60% after the cofeeding of CO or CO₂ was obtained from partial pressures higher than 4 kPa (Fig. 11a). Fig. 11b confirms these results considering the amount of water formed. Similarly, the selectivities of cracking and isomerization are changed irreversibly in favour of the isomerization over cracking. The selectivity towards isomerization is increased to about 80% for the greatest pressure of

oxygenate molecules applied (9 kPa) (Fig. 12a) depending on the partial pressure of oxygenates and depending on the partial pressure of water liberated (Fig. 12b). In addition, the hydrogenolysis activity of the platinum (followed by the production of methane) declined significantly (Fig. 12c). Therefore, the acid and hydro-dehydrogenated functions of the catalyst are irreversibly affected and the initial balance of the catalyst changed when the amount of water produced increases. Characterizations of the catalyst after the injection of oxygenated compounds confirmed that platinum dispersion (Fig. 13a) and Brønsted acidity (Fig. 13b) of the catalyst were changed. Such as acid and metal functions were both affected by the presence of oxygenates, it is difficult to unambiguously explain the gain of selectivity towards isomerization. However, it is suggested that this is due to a decrease of the hydrogenolysis activity of the platinum and also of the acidity of the support which may due to a partial demixing of the silicated alumina by water as suggested by Chizallet et al. [33] by DFT calculations.

5. Conclusion

The aim of this work was to establish and to understand the impact of model oxygenated compounds on the hydrocracking of a long chain *n*-alkanes produced in LT F-T process over a Pt supported over silicated alumina conventional bifunctional catalyst. We have clearly shown the negative impact of oxygenated molecules on the activity of the catalyst for the transformation of *n*-hexadecane and the positive effect on the catalyst selectivity towards isomerization. This effect is similar regardless the functionality of the molecule (decanoic acid, CO or CO₂ and alcohol) cofeeded with *n*-hexadecane. All oxygen molecules are totally and quickly decomposed under operating conditions into hydrocarbon (nonane, decane or methane) and water. These results correspond to a change in the balance between the acidic and hydro-dehydrogenation catalyst properties. Moreover, this effect is irreversible since it was not possible to restore catalyst performances after stopping the injection of oxygenated compounds in the feed. Indeed, there was a significant decrease of the activity of the catalyst for the transformation *n*-hexadecane and a change in selectivities in favour of the isomerization. Furthermore, hydrogenolysis activity of the platinum corresponding to methane formation is greatly diminished. This corresponds to a platinum sintering (increase in particle size and decrease of the dispersion). A reduction of Brønsted acidity of the catalyst induced by the presence of water was also observed. It is suggested that the modification the acid properties of the support and the platinum sintering has a positive effect on the catalyst selectivity towards isomerization.

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